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IMPROVED PROCEDURE FOR DETERMINING MALATHION RESIDUES IN STORED AGRICULTURAL PRODUCTS

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IMPROVED PROCEDURE FOR DETERMINING MALATHION RESIDUES IN STORED AGRICULTURAL PRODUCTS[1/]

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SUMMARY

Pentane was substituted for carbon tetrachloride as the extraction solvent in the analysis of malathion in various stored products. The percentage recovery of malathion from peanuts and peanut products almost doubled, and in other commodities the increased average percentage of recovery ranged from 6.5 to 16.5 percent. The minimum average percentage of recovery was 89 percent.

INTRODUCTION

Previously published procedures for determining malathion, S- [1,2-bis (ethoxycarbonyl) = ethyl] O,O-dimethyl phosphorodithioate, residues were modified because of emulsion interferences, low recoveries on products containing large amounts of fats and waxes, and the personal safety hazard involved in using carbon tetrachloride was used for sample extraction.

In the modified procedure, the malathion is extracted from the pulverized product with pentane. The malathion in the pentane-ethanol solution is hydrolized by sodium hydroxide to form sodium O,O-dimethyl dithiophosphate, which is extracted from the solvent phase with an aqueous sodium sulphate solution. Ferric chloride is added to oxidize interfering substances. Cupric sulphate is added to react with O,O-dimethyl dithiophosphate and form a yellow complex, which is extracted into carbon tetrachloride and measured by a spectrophotometer at 420 millimicrons. The corresponding amount of malathion is then determined by comparison with a standard curve prepared from known amounts of pure malathion carried through the procedure.

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MATERIALS AND METHODS

Extraction

Paper

Cut 0.25-sq. ft. sample, composed of three 4- by 3-in. pieces, and extract with 400 ml. of pentane for 3 hr. by tumbler (10 r.p.m.) or 1/2 hr. by shaker. Filtering is unnecessary.

Peanut Oil

A maximum of 50 g. can be run without a cleanup. Weigh this amount and transfer it with pentane to the separatory funnel.

Beans or Wheat

Use 200 g. to 400 ml. of pentane and extract by tumbler for 3 hr.

Peanuts or Cured Tobacco

Use 200 g. to 800 ml. of pentane. Extract as for wheat.

Cleanup

Cured Tobacco

Fill chromatographic tube to 12 cm. with Florisil (60-200 mesh), containing 2.5 percent water; collect eluate in 250-ml. Erlenmeyer flask. Wet column with pentane, then transfer sample aliquot (maximum of 100 ml.) to column. Rinse inside walls of column with pentane. Elute column twice with 50-ml. portions of ether (anesthesia grade) and pentane (pure grade) (1:1 mixture). Concentrate eluate carefully to dryness on steam bath under a stream of air. Dissolve residue in pentane and transfer to 250-ml. separatory funnel for analysis.

ANALYSIS

The analysis should be run as rapidly as possible to prevent degradation of the O,O-dimethyl dithiophosphate. Six samples can be run simultaneously. Transfer an aliquot containing 100-180 μg. of malathion to a 250-ml. separatory funnel and dilute to a total volume of 100 ml. Add 1 ml. of carbon disulphide (1 percent in hexane) and 25 ml. of ethyl alcohol (anhydrous, absolute) and swirl to mix. Add 75 ml. of 8.5 percent sodium sulphate (acidified with 2.5 ml. of concentrated HCl) and shake for 1 minute. Drain off and discard aqueous phase. Add 3 drops of phenolphthalein (1 percent in ethyl alcohol) and 25 ml. of ethyl alcohol and swirl to mix. Add 1 ml. of sodium hydroxide (6N) and shake for exactly 1 minute. Immediately add 75 ml. of 8.5 percent sodium sulphate (nonacidified) and shake for exactly 1 minute. (If the phases do not separate rapidly, add 5 ml. of sodium chloride, saturated aqueous solution, and shake lightly for 5 seconds.) Transfer the aqueous phase to a second separatory funnel and discard the solvent phase. Add 25 ml. of carbon tetrachloride and carefully neutralize with 6N hydrochloric acid. Add 1 ml. of ferric chloride solution (5 percent in HCl), shake for 30 seconds, allow the phases to separate, and discard the solvent phase.

Wash the aqueous phase with carbon tetrachloride two or more times until the solvent phase is colorless. After discarding the final solvent phase, add, by pipette, 20 ml. of carbon tetrachloride and 1 ml. of cupric sulphate solution (3.5 percent aqueous). Shake for 1 minute to develop color. Filter solvent phase through cotton plug into colorimeter tubes (matched Beckman or equivalent) and read at 420 millimicrons on Beckman model B spectrophotometer (or equivalent). Determine the malathion present by comparison with a standard curve (prepared from pure malathion reference standard).

RESULTS AND DISCUSSION

The percentage recovery of malathion from peanuts and peanut products was almost doubled when pentane was substituted for carbon tetrachloride (Table 1). In dry beans, flour, and wheat, the average increased percentage of recovery ranged from 6.5 to 16.5 percent. The minimum average percentage recovery when pentane was used was 89 percent for cured tobacco.

The range of recoveries when pentane is used generally is more consistent than when carbon tetrachloride is used.

This procedure is more suitable for high fat commodities than the GLC method. Twenty-four samples per day can be analyzed, and usually no cleanup is required except to recover low residues on cured tobacco. Residues may be determined more cheaply than by GLC methods.

Using this procedure, analyses can be made on six samples in 15 to 30 minutes less time than with previously published procedures because the phases separate more rapidly, which prevents degradation of the O, O-dimethyl dithiophosphate.

These data show that substituting pentane for carbon tetrachloride in the extraction procedure results in a greatly improved analytical method for determining malathion in stored foods and tobacco.

TABLE 1.--Recovery of malathion from various commodities, pentane or carbon tetrachloride as the extraction solvent[1/]

Commodity	Solvent	Replication	P.p.m.		Recovery	
			Added	Recovered	Total	Average
					Percent	Percent
Peanuts, whole	Pentane	A	0.51	0.43	86	
		B	1.02	.94	92	
		C	3.00	3.00	100	92.7
	Carbon tetrachloride	A	1.00	.30	30	
		B	1.00	.30	29	
		C	1.00	.70	70	43.0
Peanuts, shelled	Pentane	A	1.04	1.04	100	
		B	2.08	2.14	103	
		C	2.08	2.14	103	102.0
	Carbon tetrachloride	A	3.60	1.50	40	
		B	11.40	6.10	53	
		C	12.10	9.20	76	56.3
Peanut oil	Pentane	A	1.02	1.00	98	
		B	2.00	1.80	90	
		C	2.04	2.08	102	96.7
	Carbon tetrachloride	A	1.00	.39	39	
		B	1.00	.58	58	
		C	10.00	7.50	75	57.3

TABLE 1.--Continued

Commodity	Solvent	Replication	P.p.m.		Recovery	
			Added	Recovered	Total	Average
					Percent	Percent
Beans, dry	Pentane	A	1.02	1.04	102	
		B	5.00	4.70	94	98.0
	Carbon tetrachloride	A	1.04	.96	92	
		B	2.08	1.90	91	91.5
Flour	Pentane	A	2.00	2.00	100	
		B	5.00	4.70	94	97.0
	Carbon tetrachloride	A	1.04	.73	70	
		B	2.08	1.90	91	80.5
Wheat	Pentane	A	1.04	.96	92	
		B	1.60	1.58	99	95.5
	Carbon tetrachloride	A	1.04	.88	85	
		B	2.08	1.90	91	88.0
Tobacco, cured	Pentane	A	1.03	.91	88	
		B	4.00	3.60	90	89.0
	Carbon tetrachloride	A	1.03	(2/)	(2/)	
		B	4.00	(2/)	(2/)	(2/)

1/ Except for tobacco, no cleanup procedure used.

2/ No malathion recovered.